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CHARACTER OF THE INTERACTION OF ZIRCONIUM DIOXIDE WITH TITANIUM, NIOBIUM, AND CHROMIUM CARBIDES

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Studies on the mechanism of interaction of a monoclinic modification of zirconium oxide with transition metal carbides (titanium, niobium, and chromium), with the aim of finding refractory materials with improved properties, are described. Percentual compositions of the starting materials and the interaction products are tabulated. Interaction in the system ZrO_2-TiC starts at 1300°C leading, at 1900 - 2000°C, to formation of a complex oxycarbide with a lattice constant of 4.43 Å. The system ZrO_2-NbC starts interaction at 1500°C and forms a complex carbide plus a complex oxide at 1900 - 2000°C. Interaction in the system ZrO_2-Cr_3C_2 with a higher carbon content leads to reduction of ZrO_2 to ZrC and formation of Cr_7C_3. The differences in interaction are attributed to the difference in electronic structure of the carbide-forming metals of groups IV, V, VI.

As indicated earlier (Ref.1), an investigation of the mechanism of interaction of the carbides of transition metals of groups IV-VI of Mendeleyev's periodic table with refractory oxides is of interest for finding new materials with enhanced properties.

The present investigation had the purpose of studying the interaction of titanium, niobium, and chromium carbides with zirconium oxide.

As starting materials we used a monoclinic modification of zirconium oxide and carbides whose compositions are given in Table 1.

Pellets of mixtures of zirconia and carbide of the corresponding metal were heated in a vacuum of 10^{-2} mm Hg in the 1000 - 2000°C temperature range. The results of the experiments were estimated from the data of phase chemical and X-ray diffraction analyses.

At 1300°C, zirconium oxide does not interact with titanium carbide and the reaction product according to the data of chemical and X-ray analyses consists of TiC and ZrO_2 (Table 2). With a rise in temperature, the percentage of insoluble residue (ZrO_2) decreases, and the solution contains, along with titanium, /1522 a small quantity of zirconium whose content increases with the temperature. The X-ray diffraction patterns of the reaction products showed lines of a new phase; at 1900°C the X-ray patterns consisted exclusively of the lines of this phase.

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* Numbers given in the margin indicate pagination in the original foreign text.

TABLE 1

COMPOSITIONS OF CARBIDES USED

Carbide	Content, %						Sum, $M + C_{total}$
	Calculated		Based on Chemical Analysis				
	M	C	M	C_{total}	C_{bound}*	C_{free}	
TiC	80.0	20.0	79.9	19.8	19.1	0.8	99.7
NbC	88.6	11.4	88.8	11.7	11.3	0.5	100.5
Cr_3C_2	86.7	13.3	86.4	13.4	13.2	0.2	99.8

*C_{bound} was calculated for the carbide phase $= \frac{C_{total} - C_{free}}{100 - C_{free}} \cdot 100\%$.

TABLE 2

COMPOSITION OF THE PRODUCTS OF INTERACTION OF ZrO_2 WITH TiC
(Pressure, 5×10^{-2} mm Hg; heating time, 1 hr)

Temperature, °C	Content, %					Composition of Insoluble Residue, %				Composition of Solution, %				Data of X-Ray Analysis
	Ti	Zr	C_{total}	C_{free}	H/O	Ti	Zr	C	O	Ti	Zr	C	O	
Charge	39.5	37.6	10.0	0.47	50.7	Undetected	74.0	Undetected	26.0	80.0	Undetected	20.3	Undetected	$ZrO_2 + TiC$
1000	39.5	38.0	9.8	Undet.	50.6	» »	74.0	» »	26.0	79.8	» »	19.8	» »	$ZrO_2 + TiC$
1100	39.6	37.7	9.6	» »	50.9	» »	74.0	» »	26.0	80.8	» »	19.5	» »	$ZrO_2 + TiC$
1200	39.5	37.6	9.6	» »	50.8	» »	74.0	» »	26.0	81.1	» »	19.5	» »	$ZrO_2 + TiC$
1300	39.6	37.9	9.7	» »	46.0	» »	74.0	» »	26.0	73.1	7.5	18.0	1.5	$ZrO_2 + TiC$ + Traces b $a_b = 4.67$ Å
1500	39.5	38.0	9.0	» »	37.8	» »	72.8	» »	27.2	63.5	17.7	14.4	4.4	Same $a_b = 4.63$ Å
1600	39.6	33.2	8.45	» »	29.6	» »	—		—	55.1	24.1	11.8	9.0	» » $a_b = 4.58$ Å
1800	39.6	40.0	8.00	» »	19.6	» »	74.0	» »	26.0	49.1	31.9	9.95	9.1	—
1900	39.5	40.3	8.15	» »	18.1	» »	73.4	» »	26.6	47.9	33.8	9.95	8.4	b, $a = 4.43$ Å
2000	39.4	40.3	8.10	» »	10.7	» »	—	—	—	44.5	36.9	9.1	9.5	b, $a = 4.43$ Å
2200	39.5	40.0	9.0	» »	2.5	—	—	—	—	40.5	39.1	9.2	11.2	—

The new phase, conditionally called the c-phase, has a face-centered cubic lattice of the NaCl structure. The lattice constant decreases with a rise in temperature and, at 1900 - 2000°C, reaches a minimal value of a = 4.43 Å. This lattice constant does not correspond to its value for TiC (4.34 Å). Since the X-ray diffraction patterns of specimens obtained at 1900° and 2000°C do not have lines of other phases except the c-phase and since the content of insoluble residue is low at these temperatures, we can assume that the soluble part represents the c-phase. Its composition according to chemical analysis data corresponds to oxycarbide $(Zr_{0.3}Ti_{0.7}) \cdot (C_{0.56}O_{0.44})$.

When zirconium oxide was heated with niobium carbide to 1400°C no changes were observed in the composition of the starting product (Table 3).

The stability of niobium carbide in a mixture of acids with oxidizing agents and in a mixture of oxidizing agents with complexing agents was studied

to develop a method of phase analysis of the alloys of this system. It was established that niobium carbide is completely dissolved in 30% solution of hydrogen peroxide at the boiling point within 1 - 1.5 hr, and in a mixture of 30% solution of hydrogen peroxide with citric, oxalic, and tartaric acids, Trilon B, and ammonium fluoride, within 20 min. In this case the zirconium oxide for all practical purposes is not dissolved. The possibility of separating zirconium oxide from niobium carbide by a mixture of hydrogen peroxide and citric acid was checked on artificial mixtures. The results confirmed the possibility of conducting phase analyses based on the different solubility of NbC and ZrO_2 in the indicated mixture.

TABLE 3

COMPOSITION OF THE PRODUCTS OF INTERACTION OF ZrO_2 WITH NbC
(Pressure, 5×10^{-2} mm Hg; heating time, 1 hr)

Temperature, °C	Content, %					Composition of Insoluble Residue, %			Composition of Dissolved Portion, %				Phase Composition
	Nb	Zr	C_{total}	C_{free}	H/O	Nb	Zr	C	Nb	Zr	C	O	
Charge	55.1	27.9	7.30	Undetected	—	Undetected	—	—	—	Undetected	—	—	ZrO_2 + NbC a_{NbC}=4.45 Å
1000	55.0	26.9	7.15	» »	36.3	» »	74.3	Traces	86.9	» »	11.1	—	Same
1100	—	—	7.20	» »	36.4	» »	74.2	Same	86.9	» »	11.2	—	Same
1200	55.0	27.3	7.10	» »	36.5	» »	74.0	» »	87.4	» »	11.1	—	Same
1300	55.8	27.0	6.90	» »	36.6	» »	74.0	» »	87.1	» »	11.0	—	Same
1400	56.1	26.9	6.40	» »	33.4	» »	—	» »	83.2	3.15	9.8	3.85	Same a_{NbC} = 4.44 Å
1500	55.8	27.0	6.50	» »	33.3	» »	—	» »	83.2	3.22	9.8	3.78	Same a_{NbC} = 4.45 Å
1600	56.0	27.0	6.40	» »	32.5	» »	74.1	» »	83.0	4.07	9.5	3.43	Same a_{NbC} = 4.45 Å
1700	—	27.2	6.55	» »	31.3	—	—	» »	—	5.24	9.6		Same a_{NbC} = 4.44 Å
1800	27.0	27.0	6.60	» »	31.7	» »	74.3	» »	82.3	5.27	9.7	2.73	Same a_{NbC} = 4.44 Å
1900	—	27.0	5.80	» »	30.1	» »	74.2	» »	81.6	6.53	8.4	3.42	Same a_{NbC} = 4.44 Å
2000	—	26.8	5.85	» »	29.5	—	—	» »	81.0	6.24	8.3	4.46	Same a_{NbC} = 4.44 Å
2100	57.5	28.1	5.25	» »	42.8	26.2	45.2	» »	23.1	13.8	9.2	—	ZrO_2 + NbC Lines broaden, new reflections appear

The procedure of phase analysis reduces to the following: A sample of powder of 40 μ particle grain size is treated with a mixture of 50 ml 30% hydrogen peroxide solution and 30 ml of a 50% citric acid solution, under boiling for 1 - 1.5 hrs. The concentration of hydrogen peroxide is kept constant by periodically adding 3 - 5 ml. After heating, the solution is cooled, the insoluble residue is filtered off, washed, dried, and weighed.

Of the insoluble residue, 0.03 - 0.05 gm is fused with potassium pyrosulfate, the alloy is leached with a mixture of 15 - 20 ml sulfuric acid (1:4) and 1 ml of a 3% hydrogen peroxide solution; at an acidity of the solution corresponding to 2 N, the zirconium content is determined by the complexometric method. From the second portion of the insoluble residue, after fusing with potassium pyrosulfate and leaching in 15 - 20 ml of a 5% tartaric acid solution, the niobium content is determined by the colorimetric method (thiocyanate). The carbon content is determined from a third part of the insoluble residue.

The content of zirconium and niobium is determined in the solution.

Zirconium, whose content increases with the temperature of the reduction reaction while that of niobium decreases, enters into solution at 1400°C. However, up to 2100°C only lines of ZrO_2 and NbC are observed on the X-ray /1523 diffraction patterns of the reaction products. We can assume that in the system ZrO_2–NbC new phases are formed at temperatures above 1400°C but that their negligible content cannot be detected by X-ray analysis. On the X-ray diffraction patterns of the reaction products the lines broaden at 2100°C, and additional reflections appear.

In the insoluble residue, we found 26.2% Nb along with zirconium. The composition of the residue must be refined and is approximately extracted according to the formula $Nb_{0.33}Zr_{0.6}O_2$, and of the soluble part, $Nb_{1.08}Zr_{0.18}C$.

The interaction of zirconium oxide with chromium carbide Cr_3C_2 having a higher carbon content was estimated by X-ray analysis*. At temperatures up to 1300°C, lines of Cr_3C_2 and ZrO_2 are observed on the X-ray patterns of the specimens. At 1300°C, weakening of the lines of ZrO_2 and appearance of the lines of ZrC and Cr_7C_3 are observed. At 1700°C, the main phase is the ZrC phase with a lattice constant a = 4.675 - 4.676 Å, in addition to Cr_7C_3 and, in negligible quantities, Cr_3C_2 and ZrO_2. At 1800°C, the lines of ZrO_2 are absent from the X-ray patterns.

Thus, we can assume that the interaction of zirconium oxide with carbides occurs over the equations:

$$ZrO_2 + TiC \rightarrow Zr_xTi_{1-x}C_yO_{1-y}$$
$$ZrO_2 + NbC \rightarrow Nb_xZr_{1-x}C + Nb_yZr_{1-y}O_2$$
$$5ZrO_2 + 21Cr_3C_2 = 5ZrC + 9Cr_7C_3 + 10CO$$

The formation of complex oxycarbides during the reaction of ZrO_2 with TiC has to do with the fact that both these metals whose atoms, in the isolated state, have the electronic configuration d^2s^2 produce a high statistical weight of the d^0 states, with transition of some of the valence electrons to a collective state and with stabilization as a result of these valence electrons of sp^3 configuration of carbon and the formation of stable s^2–p^6 configurations of the oxygen atoms (Ref.2).

During reaction of ZrO_2 with NbC, the high statistical weight of the d^5 states of niobium causes a lessening in stabilization of the carbon atom sp^3 configurations by the valence electrons of niobium; this reduces the probability of oxycarbide formation so that a complex carbide of zirconium-niobium is formed along with the complex oxide.

This mechanism is further intensified during interaction of ZrO_2 with Cr_3C_2, i.e., with the carbide of a metal whose statistical weight of the d^5 states is still greater at a respectively lower probability of stabilization of the carbon sp^3 states and the oxygen s^2p^6 states by the chromium valence electrons. Thus, the reaction in this case proceeds under formation of only the carbides of zirconium and chromium and the removal of some of the carbon as CO

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* The X-ray analysis was performed by O.T.Khorpyakov.

with no formation of oxycarbides.

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CONCLUSIONS

The interaction in the systems ZrO_2-TiC, ZrO_2-NbC, ZrO_2-Cr_3C_2 was studied. It was established that:

The interaction in the system ZrO_2-TiC begins at 1300°C and leads, at 1900 - 2000°C, to the formation of a c-phase which is identified from the data of X-ray and chemical analyses as a complex oxycarbide of the approximate composition $(Zr_{0.3}Ti_{0.7})(C_{0.56}O_{0.44})$ with a lattice constant a = 4.43 Å.

The interaction in the system ZrO_2-NbC begins at 1500°C. At temperatures of about 1900 - 2000°C a complex carbide of the type $(Nb_xZr_{1-x})C$ is formed along with a complex oxide of the type $(Nb_yZr_{1-y})O_2$.

A chemical phase in the analysis based on the different solubility of zirconium oxide and niobium carbide in mixtures of hydrogen peroxide and citric acid was developed.

The interaction of zirconium dioxide with chromium carbide Cr_3C_2 with a higher carbon content occurs at temperatures as low as 1300°C, with the reduction of ZrO_2 to ZrC and the appearance of a lower chromium carbide Cr_7C_3.

The difference in the character of the interaction of zirconium oxide with carbides of metals of groups IV, V, and VI of the Mendeleyev periodic table is related with the difference of the electronic structure of the atoms of the metals forming the carbides.

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